

TOTAL MAXIMUM DAILY LOAD (TMDL)

For The Pesticide Fipronil in the Calcasieu River Basin

SUMMARY TABLE

Louisiana Standards Segment	Subsegment 030701: Bayou Serpent
Parameter of Concern	Pesticides (fipronil)
Uses Affected	propagation of fish and wildlife
Geographic Location	Southwestern Louisiana
Size of Watershed	209 mi ²
Stream Description	Stream heavily dredged, little canopy cover, poor drainage
Land Use/Cover	Rice farming (77%), Forest Lane (12%), wetland (4%)
Identified sources	Rice farming activities
TMDL for: Fipronil	TMDL = 0.001 lb/day In addition to the TMDL values, no introduction of fipronil, which causes local concentrations to be greater than the numeric target, will be authorized. LA = 0.0008 lb/day WLA = 0 MOS = 0.0002 lb/day

TOTAL MAXIMUM DAILY LOAD (TMDL)

**For the Pesticide Fipronil
in the Calcasieu Basin for
Bayou Serpent (Subsegment 030701)**

US EPA Region 6

May 2002

TABLE OF CONTENTS

SUMMARY TABLE	i
Executive Summary	vi
List of Abbreviations	vii
1.0 Introduction.....	1
2.0 Study Area Description.....	1
2.1 General Information.....	1
2.2 Problem Statement.....	3
2.3 Water Quality Standards.....	3
2.4 Evaluating Pesticides Data.....	4
2.5 Fipronil.....	6
2.5.1 Environmental Fate.....	7
2.6 Fipronil Sources.....	7
2.6.1 Nonpoint Sources.....	7
2.6.2 Point Sources	8
3.0 TMDL Load Calculations.....	8
3.1 Current Load Evaluation.....	8
3.2 TMDL	9
3.2 Wasteload Allocation (WLA).....	9
3.3 Load Allocation (LA)	9
3.5 Seasonal Variation	10
3.3 Margin of Safety	10
4.0 Reasonable Assurance and Other Relevant Information	10
5.0 Regulatory Authority	11
6.0 Public Participation.....	12
REFERENCES	13
APPENDIX A: Recommended Freshwater Aquatic Life Protection Numeric Targets	15
APPENDIX B-1: State of Louisiana Water Quality Standards for toxics.....	16
APPENDIX B-2: Rationale for Development of Numeric Targets.....	27
APPENDIX C: LDAF Fipronil Monitoring Data (2000 & 2001).....	29
APPENDIX D: LDAF Ambient Quarterly Monitoring Data (1999-2001)	33
APPENDIX E: Response to Comments	34

LIST OF TABLES

Table 1. Land Use in Bayou Serpent, Subsegment 030701..... 3

Table 2. Results of Analysis from LDAF 2000 and 2001 Fipronil Study Data..... 6

Table 3. Results of Analysis from the LDAF Quarterly Ambient Monitoring Stations for 1999 and 2000..... 6

LIST OF FIGURES

Figure 1. Map of the Calcasieu River Basin showing coverage of sampling locations and impaired subsegment, 030701, (marked by red star)..... 2

Executive Summary

During analysis of the data from the LDAF 1999 and 2000 fipronil studies conducted across 13 Southern Louisiana rice-growing parishes, one subsegment in the Calcasieu Basin was identified as impaired due to the pesticide fipronil.

This TMDL establishes watershed level controls for the pesticide fipronil for a single newly identified subsegment, Bayou Serpent, in the Calcasieu River Basin. A pesticide target value for the pesticide fipronil was calculated. This numeric target is not the same as a water quality standard, but a numeric value that represents the Environmental Protection Agency's (EPAs) interpretation of Louisiana's water quality narrative standard for toxics as it applies to pesticides. EPA calculated this numeric target in accordance with procedures outlined in the State of Louisiana Water Quality Standards for toxics and supporting documentation submitted to EPA Region 6. Available fipronil pesticides data for four stations in the Calcasieu River Basin has been screened against this target value, with Bayou Serpent, subsegment 030701, meeting the criteria for partial support.

Fipronil is a phenylpyrazole insecticide especially effective in controlling the rice weevil. It came into use in Louisiana rice farming in 1999, after granular carbofuran was banned from use. Fipronil use in Louisiana rice farming is controversial because crawfish production has declined. Studies conducted by scientists at the LSU AgCenter in 2000 were inconclusive in determining the strength of the relationship between crawfish toxicity and fipronil. However, the results of the 2001 studies suggest water in crawfish ponds that was just released from newly planted rice fields seeded with Icon® (trade name for fipronil) is toxic to crawfish. Further results from these studies showed that Icon® in water is nearly eight times more toxic to small crawfish than large crawfish and that with large crawfish, Icon® toxicity increases with an increase in water temperature. It is possible that the use of fipronil is a contributor to lower crawfish production in rice growing areas of Southwest Louisiana. As a precaution, Aventis and LDAF issued use restrictions to address the problem. New studies are currently being planned for 2002 to further evaluate the use of fipronil in rice farming.

This TMDL is based on a fipronil numeric target appropriate for freshwater (2.3 ug/l). It is assumed that Bayou Serpent has no assimilative capacity for fipronil loading at concentrations above the numeric targets for freshwaters. The wasteload (WLA) and load allocation (LA) cumulatively for the Calcasieu River Basin should not cause or contribute to exceedances of this numeric target. Attainment of the narrative objective for toxicity and protection of the freshwater habitat and wildlife habitat beneficial uses for Bayou Serpent is expected given the application of use restrictions issued by Aventis and LDAF. Furthermore, it is expected that with the availability of herbicide-resistant rice in the next few years, water seeding won't be necessary to control red rice, which should reduce the impacts of fipronil with water seeding. In addition to the TMDL value (0.001 lb/day), no introduction of fipronil, which causes local concentrations to be greater than the numeric target, will be authorized.

List of Abbreviations

CFR	Code of Federal Regulations
CWA	Clean Water Act
EPA	Environmental Protection Agency
LA	Load Allocation
LC ₅₀	Concentration at which 50% of the test organisms die
LDAF	Louisiana Department of Agriculture and Forestry
LDEQ	Louisiana Department of Environmental Quality
MCL	Maximum Contaminant Level
MOS	Margin of Safety
TMDL	Total Maximum Daily Load
ug/L	Micrograms Per Liter
WLA	Wasteload Allocation

1.0 Introduction

Section 303(d) of the Clean Water Act (CWA) as amended by the Water Quality Act of 1987, and EPA's regulations at 40 CFR 130 require that each state identify those waters within its boundaries not meeting water quality standards. Section 303(d) of the CWA further requires that states develop TMDL management plans for water bodies determined to be water quality limited. A TMDL documents the amount of a pollutant a water body can assimilate without violating the State's water quality standards. It also allocates that load capacity to known point sources and nonpoint sources. TMDLs are defined in 40 CFR Part 130 as the sum of the individual Waste Load Allocations (WLAs) for point sources and Load Allocations (LAs) for nonpoint sources, including a margin of safety (MOS) and natural background conditions.

Bayou Serpent, Subsegment 030701, was not included on any previous 303(d) list; however, Bayou Serpent was included in the Louisiana Department of Agriculture (LDAF) 1999 and 2000 fipronil studies conducted across 13 southern Louisiana rice-growing parishes. The subsegment was found to be "partially supporting" its designated use of fish and wildlife propagation resulting in the need for TMDL development. The suspected cause of impairment is pesticides (fipronil) and the suspected source is tailwater releases from rice farming operations. This TMDL addresses pesticide (fipronil) impairment.

2.0 Study Area Description

2.1 General Information

Bayou Serpent, subsegment 030701, is part of the Calcasieu River Basin. "The Calcasieu River Basin is located in southwestern Louisiana and is positioned in a north-south direction. The drainage area of the Calcasieu Basin comprises approximately 3,910 square miles. Headwaters of the Calcasieu River are the hills west of Alexandria. The river flows south for about 160 miles to the Gulf of Mexico; the mouth of the river is about 30 miles east of the Texas-Louisiana state line. The landscape in this basin varies from pine forested hills in the upper end to brackish and salt marshes in the lower reach around Calcasieu Lake" (LDEQ, 1993). "Bayou Serpent enters the Calcasieu River upstream from the salt water barrier that prevents salt water encroachment in the upper reaches. The subsegment is located in the parishes of Allen, Jefferson Davis and Calcasieu and has a drainage area of 130,501 acres (203.9 square miles). The bayou flows generally from the northeast to the southwest within a limited forested/scrub stream corridor. Bayou Serpent has been heavily dredged and has little canopy over most of its length. Much of the area is given over to rice farming. Because of its relatively low relief and the influence of the saltwater barrier, the region is characterized by poor drainage and frequent backwater effects from the River" (LDEQ 2001). The area is sparsely populated.

Land uses for the Calcasieu River Basin, summarized in Table 1, were obtained from the Louisiana Department of Environmental Quality (LDEQ 2001).

Table 1. Land Use in Bayou Serpent, Subsegment 030701.

Coverage Type	Acres	Percent of Watershed
Agriculture land	100,364.38	76.91
Forest land	16,237.03	12.44
Wetland	5,380.10	4.12
Rangeland	4,993.05	3.83
Water	2,565.76	1.97
Urban or built-up	938.86	0.72
Barren	22.06	0.02
TOTAL	130,501.24	100.00

2.2 Problem Statement

Bayou Serpent, subsegment 030701, was not on any 303(d) list; however, it was included as part of the 2000 and 2001 LDAF fipronil study conducted in 13 rice-growing parishes in southern Louisiana to address water quality concerns regarding the use of fipronil in rice farming. This data was a subset of the data analyzed to assess the need for TMDLs for subsegments in the Mermentau and Vermilion-Teche River Basins listed in the 1999 court-ordered Louisiana 303(d) list as not fully supporting the water quality standard with “pesticides” listed as the cause of nonsupport.

While reviewing the fipronil study data from the Mermentau River Basin, it was determined that four of the stations (Figure 1, Table 2) were located in the Calcasieu River Basin. This TMDL only addresses the pesticide fipronil in the Calcasieu River Basin.

2.3 Water Quality Standards

Designated uses for Bayou Serpent include primary and secondary contact recreation, propagation of fish and wildlife and agriculture. Bayou Serpent has been heavily dredged and has numerous weirs. The practical use of the water is as a conveyance for agricultural and stormwater run-off and a source of irrigation water (LDEQ 2001).

LDEQ’s Antidegradation Policy (LAC 33:IX.1109.A) was reviewed and this TMDL is consistent with that policy.

Narrative criterion for toxic substances may be found in the Louisiana Water Quality Standards at §1113.B.5. This reads:

“No substances shall be present in the waters of the state or the sediments underlying said waters in quantities that alone or in combination will be toxic to human, plant, or animal life or significantly increase health risks due to exposure to the substances or consumption of contaminated fish or other aquatic life. The numerical criteria (LAC 33:IX.1113.C.6) specify allowable concentrations in water for several individual toxic substances to provide protection from the toxic effects of these substances. Requirements for the protection from the toxic effects

of other toxic substances not included in the numerical criteria and required under the general criteria are described in LAC 33:IX.1121. “

Criteria for toxic substances may be found in the Louisiana Water Quality Standards at §1113.C.6. This reads:

6b. The criteria for protection of aquatic life are based on acute and chronic concentrations in fresh and marine waters as specified in the EPA criteria documents and are developed primarily for attainment of the fish and wildlife propagation use. Where a specific numerical criterion is not derived in EPA criteria documents, a criterion is developed by applying an appropriate application factor for acute and chronic effects to the lowest LC50 value for a representative Louisiana species.

6c. Criteria for human health are derived using EPA guidelines, procedures, and equations for water bodies used as drinking water supplies and those not used as drinking water supplies. Criteria applied to water bodies designated as drinking water supplies are developed to protect that water supply for human consumption, including protection against taste and odor effects, to protect it for primary and secondary contact recreation, and to prevent contamination of fish and aquatic life consumed by humans. Criteria for water bodies not designated as drinking water supplies are developed to protect them for primary and secondary contact recreation and to prevent contamination of fish and aquatic life consumed by humans. In some cases, the maximum contaminant levels (MCLs) from the National Drinking Water Regulations, when more restrictive, are used as the criteria. For those toxic substances that are suspected or proven carcinogens, an incremental cancer risk level of 10⁻⁶ (1 in 1,000,000) is used in deriving criteria, with the exception of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and hexachlorocyclohexane (lindane, gamma BHC), in which case 10⁻⁵ (1 in 100,000) is used to derive the criteria.

2.4 Evaluating Pesticides Data

As previously mentioned, Bayou Serpent was found to be “partially supporting” its designated use of fish and wildlife propagation resulting in the need for TMDL development. The suspected cause of impairment was pesticides. A primary presumption was made that Bayou Serpent’s impairment status was based on concerns that the LDEQ water quality standard addressing no toxics in toxic amounts was being violated. It is not possible to develop a TMDL for a generic listing of pesticides. Therefore one of the first steps was to establish which, if any, pesticide may be contributing to impairment of the listed subsegments. LDEQ has adopted numeric criteria for a number of pesticides, including; Aldrin, Chlorodane, DDT, TDE (DDD), DDE, Dieldrin, Endosulfan, Endrin, Heptachlor, Lindane and Toxaphene. It was recognized that this list of pesticides is very limited and does not fully represent concerns from currently used pesticides. A procedure for identifying current pesticide concerns was developed using LDAF pesticide monitoring program information.

The LDAF data set targets pesticides for monitoring according to crop types in the watershed above each established station. The LDAF monitoring program targets pesticides for monitoring by establishing crop types for a given area and then a generating a list of the pesticides approved for use on those crops. It was determined that this list would be representative of pesticides reasonably expected to be present and would define the basis list for further pesticide evaluations.

Once a pesticide has been identified, a numeric target value for that pesticide which distinguishes between the impaired and unimpaired state of the waterbody must be established. A number of the identified pesticides do not have state adopted water quality standards. In the absence of numeric criteria for these pesticides (Appendix A), a numeric target needed to be developed. These numeric target values do not represent a water quality criterion or standard; rather, they are a numeric target used to assess if a water body would be reasonably expected to be impaired based on the state's no toxics in toxic amounts narrative criterion. These numeric target values were established in accordance with procedures outlined in the State of Louisiana Water Quality Standards for toxics and supporting documentation submitted to EPA Region 6 (Appendix B-1). A more comprehensive description can be found in Appendix B-2 "Rationale for Development of Screening Levels in Louisiana 303(d) Streams Listed for Pesticides".

Two data sets were available to provide data that were considered in determining if a subsegment was indeed impaired due to pesticides. These include the LDAF fipronil study data (2000 – 2001) for the Calcasieu River Basin and LDAF quarterly ambient monitoring station network data from 1999 through 2000. LDAF conducted a study of fipronil toxicity in the Mermentau and Calcasieu River Basins in response to reports of low crawfish production in 1999 possibly due to the use of Icon®, the trade name for fipronil. Twenty-three stations throughout the rice belt were (19 in the Mermentau River Basin and 4 in the Calcasieu River Basin) sampled weekly from March through August in 2000. The water column samples were analyzed for concentrations of fipronil and its metabolites. In 2001, a follow up study was undertaken on eleven of the same stations (10 in the Mermentau River Basin and 1 in the Calcasieu River Basin) and one new station in the Mermentau River Basin. Weekly water column samples were collected beginning in March 2001 and continuing until no detects were observed at any of the stations or August, whichever came first. These data (Appendix C) were reviewed for exceedances of the freshwater acute and chronic fipronil numeric targets of 4.6 ug/l and 2.3 ug/l, respectively. Results of the review for the Calcasieu Basin are shown in Table 2. Results from the Mermentau River Basin data are addressed in a separate TMDL entitled "Total Maximum Daily Load (TMDL) for the Pesticide Fipronil in the Mermentau River Basin" (EPA, 2001).

LDAF also routinely monitors for pesticides on a quarterly basis at two fixed stations in the Calcasieu River Basin: SM-S-C-01 Calcasieu River at Hwy 190 and WM-S-C-02 Houston River @Hwy 27. Data from 1999 through 2000 were reviewed for pesticide exceedances of the freshwater acute and chronic numeric targets (Appendix D). Fipronil was not detected at these stations during this time period (Table 3).

Once numeric targets were established, the most recent three years (1999 – 2001) of data from each of the two data sets were reviewed with respect to the calculated numeric target values. Exceedances of either the acute or chronic numeric target values were noted for each impaired water body. If a pesticide concentration did not exceed its numeric target value or standard more than once in a three-year period, the water body was considered to be fully supporting. This is consistent with EPA 305(b) guidance (EPA, 1997) for assessing waterbodies. If a pesticide concentration exceeded its numeric target value or standard two or more times during a three year period, the percentage of samples in which this occurred was used to further

assess the water body as either partially supporting or not supporting with regard to the pesticide of concern. Water bodies identified as partially supporting or not supporting require a TMDL.

Fipronil was found in concentrations reasonably expected to be harmful to freshwater aquatic life in Bayou Serpent (Table 2) necessitating the development of a TMDL for Bayou Serpent, subsegment 030701.

Table 2. Results of Analysis from LDAF 2000 and 2001 Fipronil Study Data

Parish	Site #	Station Name	Wkly Mar - Aug 2000	Wkly Mar - Jun 2001	Exceed. per # of samples	% Exceed.	Rating
Jeff Davis	IXWM-09	Bayou Serpent @ Hwy 165	5.03	2.72 3.76	3/39	8%	PS
Cameron	IXWM-10	Black Bayou at Hwy 385	2.32		1/23	4%	FS
Allen	IXWM01*	3 mi W of Kinder, Hwy 190, Calcasieu River	0		0/23	0%	FS
Calcasieu	IXWM-02*	Houston River, Hwy 27; 2 mi N of Sulphur	0		0/23	0%	FS

* These stations are the same as the LDAF ambient monitoring stations WMSC01 and WMSC02 in Table 3 below.
FS = Fully Supporting; PS = Partially Supporting; NS = not Supporting; Greyed cells = not sampled in 2001

Table 3. Results of Analysis from the LDAF Quarterly Ambient Monitoring Stations for 1999 and 2000

Parish	Site #	Station Name	Qtrly 1999	Qtrly 2000	Exceed. per Quarterly samples	% Exceed.	Rating
Allen	WMSC01	3 mi W of Kinder, Hwy 190, Calcasieu River	0	0	0/8	0%	FS
Calcasieu	WMSC02	Houston River, Hwy 27; 2 mi N of Sulphur	0	0	0/8	0%	FS

2.5 Fipronil

Fipronil is a highly effective broad-spectrum phenylpyrazole insecticide for the control of a wide range of crop, public hygiene, amenity, and veterinary pests. Fipronil under the trade name of Icon® 6.2 FS is a commercially-applied seed treatment for rice which controls rice water weevil, seed midge, rice borers and grape colaspis up to the panicle differentiation stage of the rice. It may be applied to dry rice seed, which will be drilled or broadcast, or to pre-germinated rice after the rice has been soaked and drained (Aventis 2000).

Toxicity of fipronil to fish varies with species. It is highly toxic to bluegill sunfish, as indicated by the results of the two toxicity tests performed, which was identified as the most sensitive species, representative of Louisiana aquatic life (96 hour LC50 = 25 µg/l and 83µg/l, with a geometric mean of 45.6 µg/l). Fipronil is also toxic to a wide range of aquatic

invertebrates, highly toxic to shrimps and other crustacea and highly toxic to oysters (EPA 1996). The metabolite MB 46136 is more toxic than the parent compound to freshwater fish (3.3 times more toxic to bluegill sunfish). Metabolite 46136 is 6.6 times more toxic than the parent compound and MB 45950 is 1.9 times more toxic than the parent compound to freshwater invertebrates. Fipronil's tendency to bind to sediments and its low water solubility may reduce the potential hazard to aquatic wildlife (Harmon, et al 1996; USEPA 1996).

Studies conducted at the Louisiana State University Ag Center in 2001 "do not reveal a single cause for lower crawfish production in Southwest Louisiana, but it does point to a likely contributor – using water in crawfish ponds that was just released from newly planted rice fields seeded with Icon®" (Press Release Oct. 26, 2001; McClain 2001a). McClain (2001b) reported the muddiness of the water at the time of water seeding with Icon®-treated seed appears to be the determining factor as to whether the initial drain water following planting is detrimental to crawfish. Ottea and Romaire (2001) reported that in an aqueous solution, Icon® is nearly eight times more toxic to small crawfish than large crawfish at 25°C and that Icon® toxicity to large crawfish increases with an increase in water temperature.

2.5.1 Environmental Fate

Fipronil is stable to hydrolysis under mildly acid to neutral pH conditions, but degrades under alkaline conditions (pH). Field persistence is low to moderate in water and soil. Fipronil residues tend to stay in the upper 15 cm of the soil and exhibit low potential to leach to groundwater (EPA 1996; Tingle, et al 2000). In aquatic environments, fipronil residues rapidly move from the water to the sediment with over 95% of the residues being found in or on the sediments within one week of application (Bobe et al 1998; Stevens, et al 1998). Photodegradation produces a variety of metabolites, one of which is extremely stable (MB 46513) and is more toxic than the parent compound (EPA, 1998).

2.6 Fipronil Sources

2.6.1 Nonpoint Sources

The only known source of fipronil in the Calcasieu River Basin is its use in rice farming. Constant monitoring of the seed from treaters to sales persons to growers is required under the regulations put into effect on March 3, 2000 by LDAF (LSU News Release 2000a). Of the approximately 600,000 acres statewide planted in rice annually, 77,000 acres or 12.8% are attributed to the Jeff Davis Parish (LASS 2001) in which the Bayou Serpent watershed is located. The Bayou Serpent watershed land use analysis (Table 1) shows that 76.91% of the land area is agricultural land.

In Louisiana, the growing season ranges from mid March through September. Surface water from bayous and streams or ground water from wells is used to flood the fields prior to planting (late February until early June). Exceedances in the fipronil chronic numeric target (2.3 ug/L) for freshwater aquatic life protection occurred in April during both study years. Shortly after flooding, the seed is water planted. Once the rice seed has germinated, the water is drained and the field is flooded again. The field water is then held until two weeks prior to harvest (mid

July through September depending upon when the rice was planted) at which time it is released. It is believed that this practice contributes the greatest loads of fipronil to the system.

2.6.2 Point Sources

There are no known point sources for fipronil in the Calcasieu River Basin. A review of the discharger inventory for the Bayou Serpent watershed resulted in only 6 dischargers (Table 4) listed in the LDEQ Permit Tracking System (LDEQ 2001). Effluent from these point source dischargers in the Calcasieu River Basin is not expected to contain fipronil because its use is limited to rice farming. Therefore, concentrations of fipronil in their effluents are not expected and would be considered an enforcement issue and dealt with accordingly.

Table 4. Discharger Inventory for Bayou Serpent, Subsegment 030701

Facility	Permit #	Out-Fall #	Outfall Description	Receiving Water	Expected Flow GPD
Kinder Compressor Station	LA 0045918	1	Storm water runoff, treated sanitary from 101, equipment washwater, condensed water from air compressor system, and building floor drainage	Unnamed Ditches – Gum Bayou – Serpent Bayou	
		101	Sanitary sewage	Unnamed Ditches – Gum Bayou – Serpent Bayou	480
Fenton, Village of (STP)	LA 560102	1	Sanitary sewage	Ditch-Little Bayou-Bayou Serpent	36,000
Mobile City Campground	LA 540826	1	Sanitary sewage	Local-Bayou Serpent	6,250
Woodlawn Compressor Station	LA 0111881	1	Storm water runoff	Bayou Arceneaux	
		2	Sanitary sewage	Bayou Arceneaux	500
		3	Sanitary sewage	Bayou Arceneaux	
Rice Acres Well Pipeline	LAR 10B045	1	Unknown	Little Bayou	
Iowa Gas Plant	LA 0093921	1	Sanitary sewage	Unnamed ditch-Louisiana Irrigation Canal-Bayou Arceneaux-Calcasieu River	1,080

Source: LDEQ 2001

3.0 TMDL Load Calculations

3.1 Current Load Evaluation

Fipronil loads have been calculated using the chronic numeric target (2.3 ug/l) and stream flow. The following equation can be used to calculate fipronil load (lbs/day).

$$\text{Equation 1: } C \times 0.001 \times Q \text{ in cfs} \times 5.39 \text{ or } C \times 0.001 \times Q \text{ in MGD} \times 8.34$$

Where: C = concentration in mg/L
Q = stream flow in cfs or MGD

A traditional expression of the fipronil loading may be developed by setting one critical or representative flow and concentration, and calculating the fipronil loading using Equation 1. For the purpose of calculating current loading on this waterbody the geometric mean was calculated using the weekly LDAF fipronil study data for Bayou Serpent (Appendix C). In Bayou Serpent, the 14 weekly fipronil concentrations ranged from 0.45 ug/l to 5.03 ug/l over the collection period (Mar-Aug 2000, Mar-Jun 2001). The fipronil geometric mean concentration is 3.72 ug/l. According to the Louisiana Technical Procedures Manual (LTP September 8, 2000), the default summer (Mar-Nov) flow conditions are 0.1 cfs and winter (Dec-Feb) critical flow conditions are 1.0 cfs. The rice-growing season is February – September which is included in the summer critical season, except for February. Therefore, the summer critical flow condition of 0.1 cfs is appropriate for this TMDL. Using these values and Equation 1 it is estimated that the current loading to Bayou Serpent is 0.002 lbs/day.

3.2 TMDL

Point sources usually have a defined critical receiving stream low flow such as the 7Q10 (or Harmonic mean flow) at which the criterion must be met. For nonpoint sources it is recognized that there may be no single critical flow condition. Load reductions are only necessary when the calculated observed loading is greater than the TMDL. Equation 2 below can be used to calculate the needed reduction. Therefore, subtracting the TMDL load (0.001 lbs/day) from the observed load 0.002 lbs/day equals 0.001 lbs/day representing the needed reduction.

Equation 2. Current (observed) Load – TMDL load = Load Reduction

The load reduction value can be converted into a percent reduction using Equation 3 below. Thus, the percent reduction required is the load reduction (0.001 lbs/day) divided by the observed load (0.002 lbs/day) times 100. Therefore, a 50% reduction is needed.

Equation 3. Load Reduction / Current Load x 100 = % reduction

3.2 Wasteload Allocation (WLA)

There are no point source discharges, therefore, the WLA will be set to zero.

3.3 Load Allocation (LA)

As mentioned previously, this TMDL is written to cover Bayou Serpent in the Calcasieu River Basin. Therefore, the load allocation for a given flow can be calculated using Equation 1 and the following relationship:

(TMDL @ given flow and numeric target) – (WLA) – 20% MOS = LA

(0.001 @ 0.1 cfs) – (0.0) – 0.0002 = 0.0008 lbs/day

Therefore, the LA for Bayou Serpent is 0.008 lbs/day. The TMDL is based on a flow of 0.1 cfs. It is important to understand that the allowable TMDL loading will change with flow. In addition to the LA, no introduction of fipronil, which causes localized concentrations to be greater than the numeric target (freshwater: 2.3 ug/l) will be authorized.

3.5 Seasonal Variation

Section 303(d)(1) requires that all TMDLs be “established at a level necessary to implement the applicable water quality standard with seasonal variations. A review of the data shows that, in general, values greater than the numeric target value for freshwater and estuarine waters are more likely to occur in the month of April, which falls within the growing season. Therefore, the growing season from late February through September is identified as the critical period. Also, because it has been determined the most likely impact is from draining of rice fields and not necessarily storm water events, it is more likely that impacts will be observed during low flow conditions. For this reason, the Louisiana Technical Procedures Manual (LTP September 8, 2000) default summer (Mar-Nov) flow condition of 0.1 cfs was selected as the critical flow during the growing season.

3.3 Margin of Safety

The CWA requires that each TMDL be established with a MOS. This requirement for a MOS is intended to account for uncertainty in available data or in the actual effect controls will have on the loading reductions and receiving water quality. A MOS may be expressed explicitly as unallocated assimilative capacity or implicitly through conservative analytical assumptions used in establishing the TMDL. The MOS is not intended to compensate for failure to consider known sources. Because of the assumed critical flow and nature of the pollutant, it was determined that an explicit MOS of 20% was appropriate for this TMDL.

4.0 Reasonable Assurance and Other Relevant Information

The goal of this TMDL is to reduce fipronil concentrations in Bayou Serpent in the Calcasieu River Basin to meet the water quality objectives for toxicity and pesticides. As previously discussed, the only use of fipronil in this subsegment and in the Calcasieu River Basin is for applications for rice farming. Use restrictions, listed below, were established by Aventis and LDAF to reduce the exposure of crawfish to fipronil. Additional restrictions were established to reduce other sources of fipronil. Potential impacts of fipronil use appear to be more of a problem with water seeding than drill seeding reported Dr. Ray McClain with the LSU AgCenter (LSU AgCenter Press Release 2001). It is expected that the predominance of water seeding should change in the next few years when herbicide-resistant rice becomes available. This means farmers will be able to use herbicides to get rid of red rice and they won't have to water seed (Dr. Johnny Saichuk, LSU AgCenter rice specialist). Attainment of these targets and allocations are expected to result in attainment of the narrative objectives for toxicity and pesticides, and, hence, protect the freshwater and wildlife habitat beneficial uses in these subsegments.

Use restrictions recommended by Aventis Crop Science (Aventis) include:

- To prevent treated rice seed from drifting into crawfish ponds in production during aerial seeding, maintain a 100 foot buffer zone between crawfish ponds and the treated portion of the rice fields.
- After seeding, hold water in treated rice field for 24 hours before release into drainage ditches.
- Do not release water from treated rice fields directly into crawfish ponds.
- Do not fish or commercially grow fish, shellfish, or crawfish in treated rice fields prior to harvest.
- Do not plant leafy vegetables within one month following planting of treated rice seed.
- Do not plant root crops within five months following planting of treated rice seed.
- Do not plant small grains, other than rice, within twelve months following planting of treated rice seed.

5.0 Regulatory Authority

LDAF is the lead agency for pesticide regulatory control in Louisiana. The jurisdiction and authority of LDAF relative to pesticide matters is set out in the Louisiana Pesticide Law (Title 3 of the Louisiana Revised Statutes). Under the state regulatory system, the commissioner has the authority to adopt rules and regulations necessary to implement the provisions under this law including but not limited to rules and regulations governing the registration, distribution, sale, offering for sale, and application of pesticides. Furthermore, the commissioner has the authority to establish emergency procedures involving imminent danger to human health or the environment.

Under the Louisiana Pesticide Law, each pesticide, which is sold, offered for sale, or distributed in Louisiana, is registered annually. Proper certification is required to apply or supervise the application of any restricted use pesticide as a private applicator. Proper licensing is required for individuals who own or operate a business engaged in the applications of pesticides for a fee. A key component of enforcement is that it is illegal to make a pesticide recommendation or application inconsistent with the labeling or in violation of the EPA or state restriction on the use of that pesticide.

It is the responsibility of the commissioner to determine when the concentrations of pesticide wastes exceed promulgated federal or state standards, or when the concentrations of pesticides pose a threat or reasonable expectation of a threat to human health or to the environment. When such determinations are made, the commissioner shall decide the appropriate action to be taken.

LDAF monitors quarterly for the presence of pesticides in the waters of Louisiana. Determinations of excessive levels are based on scientific and technical information. Investigations may be conducted to facilitate such determinations. Excessive pesticide concentrations are alleviated through minimizing, mitigating, and preventing the potential for excessive levels. If necessary, appropriate enforcement actions may be taken.

6.0 Public Participation

When EPA establishes a TMDL, 40 C.F.R. § 130.7(d)(2) requires EPA to publicly notice and seek comments concerning the TMDL. EPA prepared this TMDL pursuant to the consent decree, *Sierra Club, et al. v. Clifford et al.*, No. 96-0527, (E.D. La.) signed and entered on April 1, 2002. Federal regulation requires that public notice be provided through the Federal Register and through newspapers in the local area. The Federal Register notice was issued on March 29, 2002 (Volume 67, Number 61, pages 15196 – 15198). This TMDL was also noticed in local newspapers including *The Times-Picayune* (New Orleans- statewide) and *The Lake Charles American Press*. Comments and additional information were submitted during the 30-day public comment period and revisions were not necessary. Response to comments are made available in Appendix E. EPA will provide notice that this TMDL has been made final, to the court, and to the Louisiana Department of Environmental Quality (LDEQ) and notification that it be incorporated into LDEQ's current water quality management plan.

REFERENCES

- Aventis Information Sheet. 2000. Rice Seed Treated with ICON® 6.2 FS Insecticide. Aventis Crop Science USA LP, Research Triangle Park, NC.
- Bobé, A., J.F. Cooper, C.M. Coste, and M.A. Muller. 1998. Behaviour of fipronil in soil under Sahelian Plain field conditions, *Pestic. Sci.*, 52(3), 275-281.
- EPA, 1998. Fipronil for use on Rice (Regent®, Icon®) and Pets (Frontline®). HED Risk Assessment. Chemical 129121. USEPA Washington DC 20460, USA. Office of Prevention, Pesticides and Toxic Substances. 90pp + 3 attachments.
- EPA, 1996. Fipronil Pesticide Fact Sheet. EPA-737-F-96-005. Office of Prevention, Pesticides and Toxic Substances, Washington DC, 10460. <http://www.epa.gov/fedrgstr/EPA-PEST/199...ay-12/pr-736DIR/Facts/Factsheet.txt.htm>.
- Hamon, Nicholas, Richard Shaw and Henry Yang. 1996. Worldwide development of fipronil insecticide. *Proc.-Beltwide Cotton Conf* 2:759-765.
- LASS (Louisiana Agriculture Statistical Service), USDA. 2001. 2000 Louisiana Agricultural Statistics. Baton Rouge, LA. Online publication available at <http://www.nass.usda.gov/la>.
- LDEQ, 2001. *Bayou Serpent Watershed TMDL for Biochemical Oxygen-Demanding Substances*, Office of Environmental Assessment, Environmental Technology Division, Engineering Group 2, Baton Rouge, LA.
- LDEQ, September 8, 2000. *Louisiana Total Maximum Daily Load Technical Procedures (LTP)*. Office of Environmental Assessment, Environmental Technology Division, Engineering Group 2, Baton Rouge, LA.
- LDEQ, 1999. *Environmental Regulatory Code, Part IX. Water Quality Regulations*. Louisiana Department of Environmental Quality. Baton Rouge, LA.
- LDEQ, 1993. State of Louisiana Water Quality Management Plan, Volume 6, Part A, Nonpoint Source Pollution Assessment Report. Baton Rouge, LA.
- Louisiana State University, 2000a. News Release: New Regulations Provide For Safe Planting With Icon Rice Pesticide. March 9, 2000. LSU Agricultural Center News. <http://www.agctr.lsu.edu/inws0309.htm>
- _____. 2000b. News Release: LSU AgCenter Scientist Find Possible Link Between Pesticide, Crawfish Mortality. May 15, 2000. <http://www.agctr.lsu.edu/wwwac/icon/mcclain.htm>.

- McClain, W. Ray. 2001a. Exposure of Hatchling Crawfish to a Rice Forage Crop Established by Water Seeding of Icon-treated Seed. LSU AgCenter, Rice Research Station, Crowley, LA.
- _____. 2001b. Crawfish Exposure to Rice Field Effluent and Its Components Following Planting with Icon-treated Seed. LSU AgCenter, Rice Research Station, Crowley, LA.
- Ottea, Jim, and Robert Romaine. 2001. Effects of Size and Temperature on the Acute Toxicity of Fipronil (Icon) to Red Swamp Crawfish, *Procambarus clarkii*. LSU AgCenter, Baton Rouge, LA.
- Stevens, M. M., K. M Fox, G.N. Warren, B. R. Cullis, N. E. Coombes & L.G. Lewis. 1998. An image analysis technique for assessing resistance in rice cultivars to root-feeding chironomid midge larvae (Diptera: Chironomidae). *Field Crops Research* 57 (1998) 195-207.
- Tingle, C.C.D., J. A. Rother, C. F. Dewhurst, S. Lauer & W. J. King. 2000. Health and environmental effects of fipronil. Pesticide Action Network UK Briefing Paper. London, UK. 30pp.
- USGS. 1997. *Water Resources Data - Louisiana, Water Year 1996*. U. S. Geological Survey, Water Resources Division. Baton Rouge, Louisiana. USGS-WDR-LA-96-1.
- USGS & EPA, 1995. National Land Cover Data (NLCD) for Louisiana

APPENDIX A: Recommended Freshwater Aquatic Life Protection Numeric Targets for Pesticides in Louisiana TMDL Development

CAS #	Name	Conc. (ug/l) LC50	Acute Numeric Level (ug/l)	Chronic Numeric Level (ug/l)	Species
94757	2,4-D	6,539	654	327	<i>Micropterus dolomieu</i>
15972608	Alachlor		760	76	EPA Recommended Criteria
101053	Anilazine	3	0.3	0.15	<i>Ceriodaphnia dubia</i>
1912249	Atrazine		328.6	11.56	Draft EPA Recommended Criteria
28249776	Benthiocarb	510	51	25.5	<i>Ceriodaphnia dubia</i>
314409	Bromacil	186,000	18,600	9,300	<i>Pimephales promelas</i>
1563662	Carbofuran	2.6	0.26	0.13	<i>Ceriodaphnia dubia</i>
81777891	Clomazone	34,000	3,400	1,700	<i>Lepomis macrochirus</i>
21725462	Cyanazine	12,693	1,269	635	<i>Ictalurus punctatus</i>
333415	Diazinon		0.1	0.1	Draft EPA Recommended Criteria
99309	Dichloran	1.08	0.11	0.055	<i>Lepomis macrochirus</i>
55290647	Dimethipin	20,900	2,090	1,045	Daphnia sp.
120068373	Fipronil	45.6	4.6	2.3	<i>Lepomis macrochirus</i>
2164172	Fluometuron	3,157	316	158	<i>Ameiurus melas</i>
51218452	Metolachlor		390	100	EPA Recommended Criteria
298000	Methyl Parathion	3.4	0.34	0.17	Southern House Mosquito
21087649	Metribuzin		N/A	100	EPA Recommended Criteria
2212671	Molinate	327	32.7	16.35	<i>Lepomis macrochirus</i>
27314132	Norflurazon	16,300	1,630	815	<i>Lepomis macrochirus</i>
19666309	Oxidiazon	2,400	240	120	<i>Daphnia magna</i>
40487421	Pendimethalin	280	28	14	<i>Ceriodaphnia dubia</i>
7287196	Prometryne	10,000	1,000	500	<i>Lepomis macrochirus</i>
709988	Propanil	1,540	154	77	<i>Ceriodaphnia dubia</i>
60207901	Propiconazole	2,925	292	146	<i>Lepomis macrochirus</i>
5902512	Terbacil	33,948	3,395	1,697	<i>Lepomis macrochirus</i>
59669260	Thiodicarb	27	2.7	1.35	<i>Daphnia magna</i>
55335063	Tricorpyr	4,243	424.3	212	Mayfly
1582098	Trifluralin	32.3	3.23	1.62	<i>Lepomis macrochirus</i>

LC₅₀ values used – 48 hour for invertebrates and 96 hour for vertebrates

APPENDIX B-1: State of Louisiana Water Quality Standards for toxics and supporting documentation submitted to EPA Region 6

LOUISIANA DEPARTMENT OF ENVIRONMENTAL QUALITY
OFFICE OF WATER RESOURCES
WATER POLLUTION CONTROL DIVISION
JUNE, 1989

DOCUMENTATION OF NUMERICAL CRITERIA FOR ACUTE AND CHRONIC
AQUATIC LIFE PROTECTION IN THE 1989 WATER QUALITY STANDARDS REVISION

Numerical criteria for fresh water and marine water aquatic life protection as listed in Table 1 of the proposed 1989 Water Quality Standards revision were derived from criteria documents of the Environmental Protection Agency. Aquatic life criteria for the following toxic substances were taken directly from those recommended in the EPA document Quality Criteria for Water 1986:

- | | |
|---|---|
| 1. Aldrin | 2. Chlordane |
| 3. DDT | 6. Dieldrin |
| 7. Endosulfan | 8. Endrin |
| 9. Heptachlor | 10. Hexachlorocyclohexane (gamma BHC,
Lindane) |
| 11. Polychlorinated Biphenyls,
Total (PCB's) | 12. Toxaphene |
| 13. 2, 4-Dichlorophenoxyacetic acid
(2, 4-D) | 14. 2-(2, 4, 5-Trichlorophenoxy)
propionic acid (2, 4, 5-TP, Silvex) |
| 46. Arsenic | 47. Chromium III (Tri) - Freshwater
Acute and Chronic only |
| 48. Chromium VI (Hex) | |
| 49. Zinc | |

Numerical criteria for aquatic life protection for the remaining toxic substances were not directly available from EPA and were derived from LC50 data for each toxic substance as presented in the following EPA documents; (1) Ambient Water Quality Criteria, 1980. EPA Series 440/5-80 and (2) Ambient Water Quality Criteria, 1984. EPA Series 440/5-84-85. To derive a criterion value, an application factor was multiplied by the lowest reported LC50 value for a representative Louisiana species as listed in Table 1 of the EPA criteria documents. Application factors used were those recommended in the EPA Water Quality Criteria 1972 (p. 123) and Quality Criteria for Water 1976 (p. 2, 3). This approach was developed in cooperation with Region VI EPA. For nonpersistent or noncumulative toxic substances, an application factor of 0.1 was used for acute protection and 0.05 was used for chronic protection. For persistent or cumulative toxic substances, an application factor of 0.05 was used for acute protection and 0.01 was used for chronic protection. The use of application factors provides a safety consideration to protect all life stages of a test species as well as to protect associated species that have not been tested and may be more sensitive to the tested toxic substance.

The following is a listing of the lowest reported LC50 values and representative Louisiana species utilized to derive numerical criteria.

Toxic Substance	Class ¹	Species ²	LC50 ³
4. TDE (DDD)	P	Scud Oyster	0.6 25
5. DDE	P	Planarian Oyster	1,050 14
15. Benzene	NP	Bluegill ⁴ <u>P. pugio</u>	22,490 27,000
16. Carbon Tetrachloride	NP	Bluegill T. Silverside	27,300 150,000
17. Chloroform	NP	Daphnia m. Pink Shrimp	28,900 81,500
18. Ethylbenzene	NP	Bluegill ⁵ <u>M. bahia</u>	32,000 87,600
19. 1, 2-Dichloroethane (EDC)	NP	Fathead minnow <u>M. bahia</u>	118,000 113,000
20. 1, 1, 1-Trichloroethane	NP	Fathead minnow <u>M. bahia</u>	52,800 31,200
21. 1, 1, 2-Trichloroethane	NP	Daphnia m. No data for Marine Water Species	18,000
22. 1, 1, 2, 2-Tetrachloroethane	NP	Daphnia m. <u>M. bahia</u>	9,230 9,020
23. 1, 1-Dichloroethylene	NP	Daphnia m. <u>M. bahia</u>	11,600 224,000
24. Trichloroethylene	NP	Daphnia p. <u>P. pugio</u>	39,000 2,000
25. Tetrachloroethylene	NP	Daphnia m. <u>P. pugio</u>	8,500 1,300
26. Toluene	NP	Bluegill <u>P. pugio</u>	12,700 9,500
27. Vinyl Chloride	No Aquatic Toxicity Data Reported		
28. Bromoform	NP	Bluegill Sheepshead minnow	29,300 17,900
29. Bromodichloromethane	No Aquatic Toxicity Data Reported		

Toxic Substance	Class ¹	Species ²	LC50 ³
30. Methylene Chloride	NP	Fathead minnow <u>M. bahia</u>	193,000 256,000
31. Methyl Chloride	NP	Bluegill T. Silverside	550,000 270,000
32. Dibromochloromethane		No Aquatic Toxicity Data Reported	
33. 1, 3-Dichloropropene	NP	Bluegill <u>M. bahia</u>	6,060 790
34. 2-Chlorophenol	NP	<u>Daphnia m.</u> No Data for Marine Water Species	2,580
35. 3-Chlorophenol		No Aquatic Toxicity Data Reported	
36. 4-Chlorophenol	NP	Bluegill Sheepshead minnow	3,830 5,350
37. 2, 3-Dichlorophenol		No Aquatic Toxicity Data Reported	
38. 2, 4-Dichlorophenol	NP	Bluegill No Data for Marine Species	2,020
39. 2, 5-Dichlorophenol		No Aquatic Toxicity Data Reported	
40. 2, 6-Dichlorophenol		No Aquatic Toxicity Data Reported	
41. 3, 4-Dichlorophenol		No Aquatic Toxicity Data Reported	
42. Phenol (total)	NP	<u>Daphnia m.</u> <u>P. pugio</u>	7,000 5,800
43. Benzidine	NP	Red Shiner No Data for Marine Water Species	2,500
44. Hexachlorobenzene		No Aquatic Toxicity Data Reported	
45. Hexachlorobutadiene	P	Fathead Minnow <u>P. pugio</u>	102 32
47. Chromium III	P	Oyster	10,300

1. P - persistent; application factors - 0.05 (acute), 0.01 (chronic)
NP - nonpersistent; application factors - 0.10 (acute), 0.05 (chronic)
2. First listed species for Freshwater
Second listed species for Marine Water
3. LC 50's reported in ug/L, parts per billion
4. Grass shrimp. Palaemonetes pugio
5. Mysid shrimp. Mysidopsis bahia

PROCEDURES FOR HUMAN HEALTH CRITERIA CALCULATION IN LOUISIANA

by Patrick Moore
Louisiana Department of Environmental Quality
Office of Water Resources
Baton Rouge, Louisiana
May 11, 1994

Introduction

The development of numerical criteria for human health protection follows guidance established by the U.S. Environmental Protection Agency (EPA). This guidance is established in a series of EPA documents including publications in the Federal Register. The approach used in developing the human health criteria for the Louisiana Surface Water Quality Standards was originally described in a Documentation Report for the 1989 Louisiana Water Quality Standards, prepared by the Louisiana Department of Environmental Quality, Office of Water Resources (LDEQ-OWR) in June, 1989.

The basic approach used by LDEQ-OWR to develop numerical water quality criteria for human health involves the review of toxicological data for each substance of concern in state waters. Substances of concern are derived from assessment of monitoring programs for water, fish and sediments, discharge and toxic release data, and other relevant information on state waters including the biennial state Water Quality Inventory (305(b) report). EPA's Integrated Risk Information System (IRIS) is used to establish the latest toxicological information on each substance. If the substance is designated as a carcinogen then the appropriate cancer potency slope factor (SF) is obtained; if it is designated a non-carcinogen, then the reference dose (RfD) is obtained. Bioconcentration factors (BCF) are also reviewed through appropriate data bases and updated if necessary. This information is then combined with other appropriate factors in the risk assessment formula to derive the criteria. Other factors considered in the formula include body weight, risk level, fish consumption, drinking water intake, and incidental ingestion while swimming. Categories of criteria are then developed for each toxic substance for drinking water (Public Water Supplies), non-drinking water, and non-swimming water (Secondary Contact).

For those toxic substances in which no toxicological data are available in the IRIS data base, the primary or secondary standards from the drinking water regulations, if available, may be used to provide a level of human health protection. As a special level of protection for drinking water supplies, taste and odor criteria may be used for

those substances associated with taste and odor problems.

The basic formulas, illustrated below, were obtained from a Federal Register notice, November 28, 1980. Further explanation and description of these guidelines can be found in *Assessing Human Health Risks from Chemically Contaminated Fish and Shellfish: A Guidance Manual*. The 1980 Federal Register notice established the use of 2 liters for the average water consumption and the use of 70 kilograms for an average adult body weight. Carcinogenic SFs and non-carcinogenic RfDs are obtained from EPA's IRIS. The fish consumption rate of 20 grams per day used in the formulas was obtained from the U.S. Department of Agriculture's 1984 National Consumption Statistics. A health risk level of one in a million (10^{-6}) has been established for determining criteria for carcinogens with the exception of dioxin and lindane, which have been assigned a 10^{-5} risk level. Additionally, a SF is figured into the formula if the chemical has been given a cancer classification of A, B1, B2, or C. If the chemical has not yet been shown to be a carcinogen, or, if it has been shown that it is not a carcinogen, then a RfD is used instead of a SF.

For water bodies with the designated use of primary contact recreation (swimming), an incidental ingestion rate is included in the formula. The incidental rate is given by this formula:

$$\begin{aligned} & \frac{250 \text{ ml}}{\text{hour}} \text{ possible ingestion} \times \frac{5 \text{ hrs}}{\text{wk}} \text{ swimming duration} \\ & \times \frac{6 \text{ mos}}{12 \text{ mos}} \text{ swimming season} \times \frac{1 \text{ week}}{7 \text{ days}} \\ & = 89 \times \frac{\text{ml}}{\text{day}} = 0.089 \frac{\text{liters}}{\text{day}} \text{ incidental ingestion} \end{aligned}$$

The following are descriptions of items used in the risk-based formulas:

10^{-6}	= risk level
70 kg	= average adult male body weight
BCF	= bioconcentration factor in L/kg
0.02 kg/day	= national average amount of fish/shellfish consumed daily in kilograms (20 g/day)
SF	= cancer potency slope factor in mg/kg/day^{-1}
RfD	= reference dose in mg/kg/day
2 L/day	= national average amount of water consumed daily in liters

The equation for a carcinogen in waters designated as public water supply is:

$$\text{Criteria} \frac{\text{mg}}{\text{L}} = \frac{(10^{-6}) (70 \text{ kg})}{\text{SF} [0.089 \text{ L/day} + 2 \text{ L/day} + (\text{BCF}) (0.02 \text{ kg/day})]}$$

The following equation is for a non-carcinogenic chemical in water bodies designated as public water supplies:

$$\text{Criteria } \frac{\text{mg}}{\text{L}} = \frac{\text{RfD} \times 70 \text{ kg}}{0.089 \text{ L/day} + 2 \text{ L/day} + (\text{BCF}) (0.02 \text{ kg/day})}$$

The equation for a carcinogen in waters not designated as public water supplies is:

$$\text{Criteria } \frac{\text{mg}}{\text{L}} = \frac{(10^{-6}) (70 \text{ kg})}{\text{SF} [0.089 \text{ L/day} + (\text{BCF}) (0.02 \text{ kg/day})]}$$

The equation for a non-carcinogen in waters not designated as public water supplies is:

$$\text{Criteria } \frac{\text{mg}}{\text{L}} = \frac{\text{RfD} \times 70 \text{ kg}}{0.089 \text{ L/day} + (\text{BCF}) (0.02 \text{ kg/day})}$$

The equation for a carcinogen in non-drinking waters with secondary contact recreation (no swimming use) is:

$$\text{Criteria } \frac{\text{mg}}{\text{L}} = \frac{(10^{-6}) (70 \text{ kg})}{\text{SF} [(\text{BCF}) (0.02 \text{ kg/day})]}$$

The equation for a non-carcinogen in non-drinking waters with secondary contact recreation (no swimming use) is:

$$\text{Criteria } \frac{\text{mg}}{\text{L}} = \frac{\text{RfD} (70 \text{ kg})}{\text{BCF} (0.02 \text{ kg/day})}$$

For excepted use water bodies, special procedures for calculating site-specific criteria may be used. In general, for water bodies with the primary contact recreation use removed, the incidental ingestion rate for water will also be removed from the equation. Most states do not have an incidental ingestion rate for swimmers, and, even so, most of Louisiana's human health criteria will be more stringent than other states. A use attainability analysis may show that a special water body supports only a limited fishery use. The fish population in this type of water body is not composed of typical sport fish for consumption. Instead, the fish are usually small and

inappropriate for human consumption. Therefore, for excepted use water bodies, Louisiana will use the national fish consumption rate of 6.5 grams per day, or another suitable fish consumption rate, rather than the usual 20 grams per day. Since many states use this or other fish consumption rates, Louisiana criteria for this type of water body will still be comparable to the human health criteria of other states.

Modifying the Criteria

Because toxicological information is subject to change, the scientific data must be checked periodically and updated, if necessary. Occasional comparisons of 1) EPA's IRIS and 2) the appropriate, most current criteria documents to LDEQ's human health criteria spreadsheet will facilitate any modifications to any particular criterion. If any of the criteria needs modifying, changes can most easily be made through the already established QUATTRO PRO spreadsheet.

Accessing the Spreadsheet

(Note: These instructions are written to enter the spreadsheet with a MOUSE. If one wishes to work within QUATTRO PRO strictly using his/her keyboard, he should use the ?/ key in conjunction with the arrow and ENTER key.)

To access the spreadsheet, at the C prompt type cd QPRO

At the C:\QPRO > prompt, type Q

Once in the spreadsheet, click on FILE then RETRIEVE

Click on the file named TOXICCAL.WK2

YOU ARE NOW IN THE LDEQ HUMAN HEALTH CRITERIA TABLE.

To Make Changes to Parameters

Move cursor to desired cell (parameter-column and chemical-row), type in correction, and press ENTER

Screen will blink twice and new number(s), and new criteria, will appear.

To Edit the Formulas (for columns J, K, and L)

Arrow over to either column J, K, and/or L. Press F2 then use both the ←→ keys and DELETE to make desired changes.

To keep changes, press ENTER.
(NOTE: IF YOU HAVE MADE UNDESIRABLE CHANGES, PRESS ESC TWICE
TO START EDITING PROCESS OVER.)

To Print

Click on PRINT then BLOCK.

Once in BLOCK then type A3..M58 (or the line corresponding to the last
chemical) and press ENTER.

To View New Table in Print Mode

- a) In PRINT menu, click on DESTINATION. Next click on SCREEN PREVIEW.
- b) With desired BLOCK (Axx..Nxx) entered, click on SPREADSHEET PRINT. Entire table will now appear on the screen.
- c) To see table better, click on ZOOM(+) and CLICK-DRAG Red Box to desired part of the screen to check for corrections made.
- d) Click on UNZOOM(-) then QUIT to return to PRINT menu.
- e) If part of table did not show, click on LAYOUT then PERCENT SCALING.
- f) Type in a reasonable value and press ENTER.
- g) Click on QUIT.
- h) Repeat steps b-g until desired appearance of table is achieved.

Click on DESTINATION once more; then on GRAPHICS PRINTER.

Click on SPREADSHEET PRINT.

YOUR NEW TABLE IS NOW PRINTING

To Save/Exit the Spreadsheet

IF YOU WANT TO SAVE YOUR CHANGES:

To save changes to existing file name, click on FILE menu then SAVE AS then ENTER.

IF YOU WANT TO SAVE YOUR CHANGES UNDER A NEW FILE NAME:

Follow the previous step.

Type in the new name before pressing ENTER (QUATTRO PRO REQUIRES NAME TO BE XXXXXXXX.WKX).

IF YOU DO NOT WANT ANY CHANGES SAVED AND/OR YOU WANT TO EXIT THE SPREADSHEET:

Click on FILE then EXIT.

THIS STEP WILL EXIT YOU FROM THE SPREADSHEET AND QUATTRO PRO WITHOUT SAVING ANY CHANGES MADE TO THE TABLE.

(IF THERE ARE ANY SPECIFICS YOU WANT DONE TO THE TABLE, PLEASE CONSULT THE QUATTRO PRO MANUAL.)

Table A. Calculations used to derive the proposed 1991 dioxin (2,3,7,8-TCDD) criteria for the Louisiana Surface Water Quality Standards.

ASSUMPTIONS				CRITERIA ¹	
BCF ²	FCR ³	SF ⁴	Risk Level	Drinking Water	Non-Drinking Water
5,000	20	9,700	10 ⁻⁵	0.71	0.72

¹ Criteria expressed in parts per quadrillion (ppq)

² BCF = Bioconcentration Factor (L/Kg)

³ FCR = Fish Consumption Rate (g/day)

⁴ SF = Cancer Slope Factor (mg/Kg/day)

⁵ DEQ 1989 revision includes 0.089 L/day incidental water ingestion for both drinking water and non-drinking water; an additional 2 L/day used only on drinking water

⁶ 70 Kg = Average adult body weight

$$\text{Drinking (ppq) Water} = \frac{(10^{-5})(70 \text{ kg})^6}{\text{SF} [0.089 + 2 \text{ L/day} + (5,000 \text{ L/kg})(\text{FCR kg/day})]}$$

$$\text{Non-Drinking (ppq) Water} = \frac{(10^{-5})(70 \text{ kg})}{\text{SF} [0.089 \text{ L/day} + (5,000 \text{ L/kg})(\text{FCR kg/day})]}$$

APPENDIX B-2: Rationale for Development of Numeric Targets in Louisiana 303(d) Streams Listed for Pesticides

The Environmental Protection Agency (EPA), Region 6, Water Quality Protection Division has developed numeric targets for pesticides, identified through analytical measurements, to evaluate the need for development of Total Maximum Daily Loads (TMDL) in waterbodies identified and listed as not in attainment of the State of Louisiana water quality standards, as required under §303(d) of the Clean Water Act (CWA). This action was necessary to both evaluate the need for TMDL development and as a goal when a TMDL is required. The development of the numeric targets has been performed without prior knowledge of the analytical values obtained by the Louisiana Department of Agriculture and Forestry (LDAF) through water quality monitoring. The list of analytes was reviewed by senior staff and management in the EPA Region 6, Multimedia Planning and Permitting Division, which provided Chemical Abstract Service (CAS) numbers and product names for each pesticide. Where the State of Louisiana has established water quality criteria, those criteria were used for screening. Where the EPA has developed (or drafted but not finalized) recommended aquatic life protection criteria for a pesticide, but the State of Louisiana had not adopted the criteria, the EPA recommended criteria was used as a numeric target. For all other measured pesticides numeric targets were established in accordance with the State of Louisiana Water Quality Standards and established procedures submitted to EPA Region 6.

In accordance with LAC 33:IX.1113.C.6.b., acute and chronic aquatic life values were developed, based on information contained in EPA's ECOTOX (ecological toxicity) database and from EPA's Office of Pesticides database, supplied by the Region 6 Multimedia Planning and Permitting Division, Pesticides Section. LAC 33:IX.1113.C.6.b. states;

“The criteria for protection of aquatic life are based on acute and chronic concentrations in fresh and marine waters as specified in the EPA criteria documents and are developed primarily for attainment of the fish and wildlife propagation use. Where a specific numerical criteria is not derived in EPA criteria documents, a criterion is developed by applying an appropriate application factor for acute and chronic effects to the lowest LC₅₀ value for a representative Louisiana species.”

In implementing this provision EPA reviewed the available data and used the lowest 48-hour LC₅₀ values for invertebrate species indigenous to Louisiana, and the lowest 96-hour LC₅₀ values for vertebrate species indigenous to Louisiana. EPA utilized application factors of 0.1 for acute criteria and 0.05 for chronic criteria, in accordance with the document submitted to EPA Region 6 “*Documentation of Numerical Criteria for Acute and Chronic Aquatic Life Protection in the 1989 Water Quality Standards Revisions*”, dated June 1989. Where multiple data points were available the geometric mean was utilized for test data points. Data from different sources was evaluated to determine if concentrations were measured analytically or were based on a formulation and a dilution calculation, with a preference for measured concentrations. However; if only calculated concentrations were available, based on formulated products and calculated concentrations, that data was used in determining the acute and chronic numeric targets (products of LC₅₀ and application factor).

For the compound Fipronil EPA contacted the US Department of Agriculture and Louisiana State University (LSU) to obtain information concerning the effects of Fipronil to crayfish, based on complaints of the adverse effects this pesticide was having on crayfish farming. At this time LSU is conducting toxicity tests using crayfish and examining the effects on different life stages and size. Because some of the degradation products of Fipronil are more toxic than the parent compound, establishing a numeric target that considers the toxicity of the parent compound and the degradation products will be difficult and time consuming. For the purpose of this activity, data from the EPA database was used in establishing a numeric target for aquatic life protection.

No calculations were necessary for pesticides that have Louisiana adopted water quality criteria for aquatic life protection or for EPA recommended water quality criteria for the protection of aquatic life. Numeric targets developed for the remaining pesticides were established using the following formulae:

$$\text{Acute numeric target} = (\text{LC}_{50}) \times 0.1$$

$$\text{Chronic numeric target} = (\text{LC}_{50}) \times 0.05$$

Example Calculation:

$$\begin{aligned} \text{Acute numeric target for fipronil} &= 45.6 \mu\text{g/l (LC}_{50} \text{ for } \textit{Lepomis macrochirus}) \times 0.1 \\ &= 4.6 \mu\text{g/l} \end{aligned}$$

$$\begin{aligned} \text{Chronic numeric target for fipronil} &= 45.6 \mu\text{g/l (LC}_{50} \text{ for } \textit{Lepomis macrochirus}) \times 0.05 \\ &= 2.3 \mu\text{g/l} \end{aligned}$$

APPENDIX C: LDAF Fipronil Monitoring Data (2000 & 2001)

* Samples analyzed for Fipronil and Metabolites #46136, #46513 and #45950

Water Monitoring Results for Fipronil[□] -Calcasieu River Basin, Louisiana 12/31/2000											
Parish, Site #, Location	Week of 03-06-00	Week of 03-13-00	Week of 03-20-00	Week of 03-27-00	Week of 04-03-00	Week of 04-10-00	Week of 04-17-00	Week of 04-24-00	Week of 05-01-00	Week of 05-08-00	Week of 05-15-00
Allen, IXWM-01 3 mi. West of Kinder, Hwy 190, Calcasieu River	ND-ALL	ND-ALL	F: 0.23 Others: ND	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ns
Calcasieu, IXWM-02 Houston River, Hwy 27; 2 mi. N. of Sulphur	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ND-ALL	ns
Jeff Davis IXWM-09 Bayou Serpent at Hwy 165	F: 1.18 Others: ND	F: 1.00 Others: ND	F: 2.03 Others: ND	ND-ALL	F: 0.47 Others: ND	F: 5.03 M#46513: 0.34 M#46136: 0.21 M#45950: ND	F: 1.26 Others: ND	F: 0.47 Others: ND	F: 0.45 Others: ND	ND-ALL	ns
Cameron IXWM-10 Black Bayou at Hwy 385	ND-ALL	ND-ALL	ND-ALL	F: 0.65 Others: ND	F: 0.53 Others: ND	F: 0.51 Others: ND	F: 2.32 M#46513: 0.36 Others: ND	F: 0.36 Others: ND	ND-ALL	ND-ALL	ns

**Continued: Water Monitoring Results for Fipronil* -Southwest, Louisiana
12/31/2000**

Parish, Site #, Location	Week of 05-22-00	Week of 05-29-00	Week of 06-05-00	Week of 06-12-00	Week of 06-19-00	Week of 06-26-00	Week of 07-05-00	Week of 07-10-00	Week of 07-17-00	Week of 07-24-00	Week of 07-31-00
Allen, IXWM-01 3 mi. West of Kinder, Hwy 190, Calcasieu River	ns	ND-ALL									
Calcasieu, IXWM-02 Houston River, Hwy 27; 2 mi. N. of Sulphur	ND-ALL	ND-ALL		ND-ALL							
Jeff Davis IXWM-09 Bayou Serpent at Hwy 165	ns	ND-ALL									
Cameron IXWM-10 Black Bayou at Hwy 385	ND-ALL	ND-ALL	ns	ND-ALL							

**Continued: Water Monitoring Results for Fipronil* -Southwest, Louisiana
12/31/2000**

Parish, Site #, Location	Week of 08-07-00	Week of 08-14-00	Week of 08-23-00
Allen, IXWM-01 3 mi. West of Kinder, Hwy 190, Calcasieu River	ND-ALL	ND-ALL	ND-ALL
Calcasieu, IXWM-02 Houston River, Hwy 27; 2 mi. N. of Sulphur	ND-ALL	ND-ALL	ND-ALL
Jeff Davis IXWM-09 Bayou Serpent at Hwy 165	ND-ALL	ND-ALL	ND-ALL
Cameron IXWM-10 Black Bayou at Hwy 385	ND-ALL	ND-ALL	ND-ALL

Water Monitoring Results for Fipronil* - Southwest, Louisiana
7-26-01

* Samples analyzed for Fipronil and Metabolites #46136, #46513 and #45950

Parish, Site # Location	Week of 03-08-01	Week of 03-15-01	Week of 03-21-01	Week of 03-28-01	Week of 04-02-01	Week of 04-09-01	Week of 04-16-01	Week of 04-23-01	Week of 04-30-01	Week of 05-07-01	Week of 05-14-01
Jeff Davis IXWM-09 Bayou Serpent at Hwy 165	ND	ND	F: 0.73 Others: ND	ND	F: 2.72 Others: ND	F: 0.99 Others: ND	F: 0.95 Others: ND	F: 0.63 Others: ND	F: 3.76 M#46513: 0.53 M#46136: 0.37 M#45950: 0.22	ND	

* Samples analyzed for Fipronil and Metabolites #46136, #46513 and #45950

Parish, Site # Location	Week of 05-21-01	Week of 05-28-01	Week of 06-04-01	Week of 06-11-01	Week of 06-18-01	Week of 06-25-01	Week of 07-02-01	Week of 07-09-01	Week of 07-16-01	Week of 00-00-01	Week of 00-00-01
Jeff Davis IXWM-09 Bayou Serpent at Hwy 165	F: ND M#46513: 0.25 M#46136: ND M#45950: 0.21	ND	ND	ND	ND	ND					

APPENDIX D: LDAF Ambient Quarterly Monitoring Data (1999-2001)

Station	Pesticide	Numeric Target ug/l	1999				2000				2001			
			1st Qtr	2nd Qtr	3rd Qtr	4th Qtr	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr	1st Qtr	2nd Qtr	3rd Qtr	4th Qtr
WM-S-C-01*														
WM-S-C-02	Atrazine	12.0					0.21							

- Data is only reported for pesticides present above the laboratory detection levels.

APPENDIX E: Response to Comments

EPA received comments from the Louisiana Department of Environmental Quality in a letter dated April 29, 2002 addressed to Ellen Caldwell. The response to comments specific to Turbidity and suspended solids only are given below.

April 29, 2002

Ms. Ellen Caldwell, Environmental Protection Specialist
Water Quality Protection Division
United States Environmental Protection Agency, Region 6
1445 Ross Avenue
Dallas, Texas 75202-2733

RE: Comments on Federal Register: March 29, 2002 (Volume 67, Number 61) [FRL-7165-6], Clean Water Act Section 303(d): Availability of Total Maximum Daily Loads (TMDLs) and Determinations that TMDLs are not needed for 20 waterbody/pollutant combinations in the Calcasieu and Ouachita river basins.

Dear Ms. Caldwell:

The Louisiana Department of Environmental Quality hereby submits comments on the 98 TMDLs and the calculations for these TMDLs prepared by EPA Region 6 for waters listed in the Calcasieu and Ouachita river basins, under section 303(d) of the Clean Water Act. Listed below are general comments. Refer to the Attachments for specific comments and discussion.

1. It is inappropriate to use non-regulatory "targets" (sediment guidelines or others) as end-points for TMDLs.
2. Incorrect flows were applied in some areas (e.g. harmonic mean was used rather than tidal flows).
3. EPA's use of non-clean technique metals data is inappropriate. Metals data from the Superfund project should not have been used at all since clean sampling and analysis techniques were not used. When EPA did use these data, they were often not applied correctly. For example, Louisiana instream criteria are based on dissolved metals; yet EPA used both dissolved and total metals data to compare to the dissolved criteria. EPA's use of applying total metals to dissolved metals criteria in order to determine exceedance is flawed.
4. LDEQ Ambient Network data should not have been used to justify TMDLs for the same reason as the Superfund data. The available LDEQ data were not collected and analyzed using clean techniques. LDEQ uses these data as a

screening tool to target more intensive sampling and analysis using clean techniques, not for justifying and developing TMDLs.

5. It is inappropriate to assume industries discharge a pollutant when it has not been included in their permit. EPA knows that when effluent limits are determined for each facility based on a number of factors, including the type of facility, types of waste-streams and effluent data submitted during the application process.
6. Monitoring schedules and locations for the different pollutants have been recommended for Louisiana throughout the document; Louisiana will continue its ambient and intensive monitoring programs according to established schedules and agreements.
7. LDEQ's comments concerning specific TMDLs will indicate that EPA has made numerous errors in listing dischargers in the TMDL.
8. The use of sediment data to assess for water quality use impairment and need for TMDLs has no precedent. Neither LDEQ nor EPA has promulgated sediment criteria. Therefore, the use of non-regulatory sediment guidelines and screening values, as Region 6 has done in this report, is not appropriate in assessing for water quality impairment or determining the need for TMDLs.
9. Many of these TMDLs are based on models using historical water quality data gathered at a single or small number of locations rather than survey data gathered at sites spaced throughout the waterbody. The hydraulic information used was generally an average value or estimated value, not taken at the same time as the water quality data. The calibrations are inadequate due to the lack of appropriate hydrologic data and the paucity of water quality data. The resulting TMDLs are invalid. LDEQ does not accept these TMDLs.

We look forward to hearing your response to these comments.

Sincerely,

Emelise S. Cormier
Environmental Scientist Senior
Technology Division

Enclosure(s)

c: Willie Lane
EPA
Region 6

LDEQ COMMENTS ON THE DRAFT TMDLS PUBLISHED BY EPA

LDEQ has reviewed the TMDLs published by EPA on March 29, 2002. One particularly troubling issue for LDEQ is the fact that numerous dischargers that should have been included in these TMDLs were not. This indicates a complete disregard for the discharger inventory LDEQ provided to EPA. At the least, the TMDLs should acknowledge all facilities present in the covered watershed(s) and present the decisions for including or not including them in the TMDL.

In the future, LDEQ requests that EPA provide hard copies of the TMDLs and Appendices for LDEQ review. Hard copies will insure that the complete official document is being reviewed and will eliminate the time required for LDEQ to put together the document from electronic files.

In general, LDEQ found these TMDLs to be unacceptable.

Federal Register Notice: Volume 67, Number 61, pages 15196 - 15198 (3/29/2002)

PESTICIDES

Ouachita River Basin TMDLs for Selected Pesticides (Subsegments 081001, 080903, 080901, 081002, 081201)

Bayou Serpent Fipronil (Subsegment 030701)

General Comments on Pesticide TMDLs:

1. The flow used for calculations should be the flow established in the LDEQ regulations rather than one rationalized by EPA. Since the TMDLs state that they must account for aquatic life and human health, the 7Q10 and the harmonic mean should have been calculated for this stream and the more stringent value should have been used to establish the TMDL. The EPA should have established the TMDL calculation using the correct flow based on the regulations and if necessary made recommendations for changes to the criteria.

Response: For the Bayou Serpent Fipronil TMDL, EPA believes the default value for flow given in the Louisiana Technical Procedures Manual and used in this TMDL is appropriate because pesticide (Fipronil) impairment in Bayou Serpent is a function of tailwater release from rice fields.

EPA believes the 7Q10 is not an appropriate flow for use with pesticides considered in the Ouachita River Basin TMDL because pesticides impairment in this basin is a function of wet weather conditions. This TMDL was written to address violations of the aquatic life use not human health concerns. EPA had determined that using the arithmetic mean is appropriate. Additionally, because flow data is not normally distributed, the arithmetic mean is not the 50th percentile but ranges from the 66th to the 70th percentile for the USGS gaging stations used in this TMDL and therefore, provides an additional level of protection.

2. The time interval for collecting data represents a time of intense agricultural activity. Data should have been collected for the entire yearly cycle at the very least. Complete understanding of the effects of the pesticides on the waterbody during the rest of the year cannot be established without it. The actual critical periods cannot be established without a complete study.

Response: With regard to the Bay Serpent Fipronil TMDL, LDAF conducted studies in the Calcasieu River Basin over 2 growing seasons. In the first year weekly data collection began in March and continued through August. In the second year, weekly data collection began in March and continued through June because no detects were observed at any of the stations since April. Fipronil should not have an effect outside of the growing season because Fipronil use is directly correlated with rice farming and the release of tailwater and both studies indicated exceedances in the Fipronil numeric target only early in the growing season (Mar and April).

With regard to the Ouachita River Basin Pesticide TMDL, due to the court-ordered deadlines, it was not possible for EPA to complete a year-long study. EPA conducted a 6-month study targeted at characterizing the conditions during a period of time when spring pesticides were being actively applied. This study provided first time data for some subsegments and supplemented existing data for stations monitored quarterly by LDAF through their ambient monitoring program. Since LDAF only monitors for currently used pesticides, the study provided data regarding the presence of banned pesticides in these subsegments. The seasonal patterns observed in all the data used in this study were typical of those patterns observed in the MISE study (Kleiss, et al, 2000).

3. A Non-agricultural activity projection was not addressed in this TMDL.

Response: As stated in the TMDLs, no known formulators of these pesticides are known to exist in these watersheds. Agriculture was considered to be a significant source for these specific pesticides because it is the primary landuse. Urban landuse in these watersheds accounts for 0.1% to 0.5% and therefore, public use of these pesticides is negligible compared to agricultural uses and was not considered to have a significant effect.